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Solid-State Phase Equilibria in the ZnS-CdS System

by

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SOLID-STATE PHASE EQUILIBRIA IN THE ZnS-CdS SYSTEM

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ABSTRACT:

The ZnS-rich region of the ZnS-CdS phase diagram, up to 18 mol % CdS, was studied over the temperature range 700 to 950 °C, and the boundaries describing the equilibria between the sphalerite and wurtzite solid solutions were determined. X-ray diffraction analysis was the principal technique used, the phase boundaries being determined by the lattice-parametric and disappearing phase methods. The results indicate that the solubility of CdS in ZnS is extensive in both the sphalerite and wurtzite phases, with CdS stabilizing the wurtzite phase.

MATERIALS INDEX: Zinc Sulfide, Cadmium Sulfide, Phase Equilibria

Introduction

The II-VI compound ZnS is technologically important due to its infrared transmitting and luminescent properties. Although many of its optical properties are adequate for various applications, there is considerable interest in improving its mechanical behavior. One method for hardening and toughening ceramic materials is by the incorporation or precipitation of a second phase in the matrix. This can be accomplished by a variety of methods, including thermal or thermo-mechanical processing to control solid-state reactions, which is the route we are pursuing. To utilize this approach a knowledge of the phase diagrams of the systems of potential interest is necessary.

ZnS is known to exist in two polymorphic modifications, sphalerite (cubic, zinc-blende) and wurtzite (hexagonal). The cubic form is stable at low temperatures and transforms to wurtzite at 1020 °C (1). The sphalerite-wurtzite (S-W) transition is affected by the addition of solutes, but knowledge of the phase equilibria is sparse. We selected the ZnS-CdS system for study because the optical properties of CdS are such that ZnS-CdS solid solutions or two-phase mixtures are likely to retain the excellent infrared transmission characteristics of pure ZnS.

CdS forms a complete series of solid solutions with wurtzite at high temperatures (T > 975 °C) (2), but the only work on the phase equilibria at lower temperatures is a study conducted under hydrothermal conditions over the temperature range 250-450 °C (3). Those conditions and temperatures, however, are not practical for the thermal processing treatments we believe are required to produce strengthening and toughening. In this investigation, the phase boundaries between the ZnS-rich sphalerite and wurtzite solid solutions were determined over the temperature range 700-950 °C.

Experimental

Samples were prepared from weighed amounts of cubic ZnS (99.9 %, Aesar) and hexagonal CdS (99.9 + %, Aesar) powder and mixed. The typical sample weighed at least 1 g, and alloys containing up to 18 mol % CdS were investigated. Approximately 0.2 g of each mixture was transferred to a silica ampoule, evacuated to 2×10^{-2} torr, and heated to 120 °C for 10 to 15 minutes to remove adsorbed water. The ampoule was then sealed and isothermally annealed at the desired temperature for times ranging from 1 to 4 weeks. X-ray diffraction analysis using monochromatic Ni-filtered CuKα radiation was employed to identify the phases present and to determine their lattice constants. The phase boundaries were evaluated by using either the disappearing phase method or the parametric method (4). The X-ray intensities were recorded digitally in a step-scanning mode at intervals of 0.01° for 1 s or 0.02° for 10 s. Either NaCl or KCl powders were used as a standard, depending upon the amount of peak overlap with the samples, to obviate the need for precise alignment of the diffractometer.

Results and Discussion

The phases detected by analysis of the peaks in the X-ray diffraction patterns in a large number of samples heat-treated at the four temperatures used in this study are presented in Fig. 1. This is a map describing the phase equilibria, in which the compositions of the phase boundaries are only approximately determined. The compositions were then determined more precisely using the X-ray methods mentioned above.
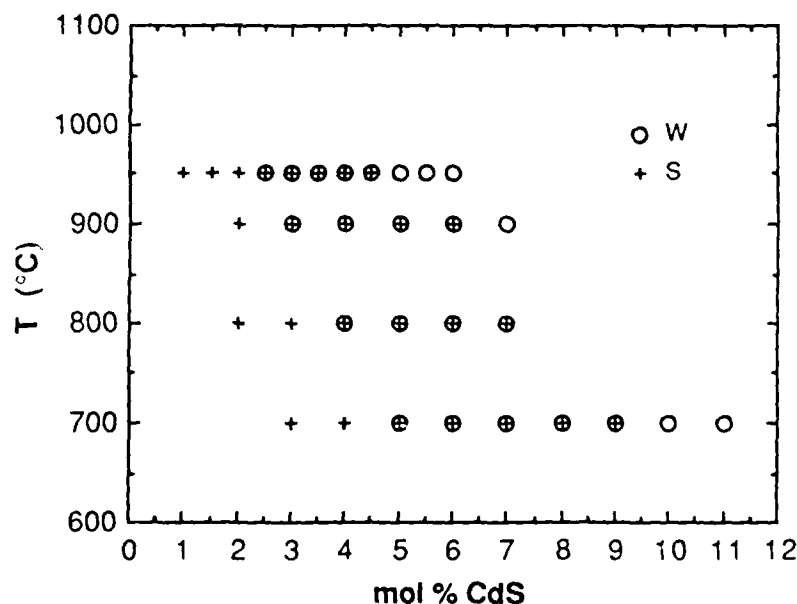

FIG. 1
Identification of the phases observed on heating mixtures of
ZnS and CdS powders for various times at the temperatures indicated.

An example of the determination of a phase boundary using the parametric method is shown in Fig. 2. In a single-phase region the lattice constant of the solid solution will vary with the concentration of solute if the atomic or ionic radii of the solvent and solute differ. Generally, this change is approximately linear and should be independent of the thermal history of the sample so long as equilibrium is reached. The solid line in Fig. 2 represents the variation of the lattice constant with composition of the sphalerite solid solution in the single-phase region. At the higher

reaction temperatures (900 and 950 °C) equilibrium was established relatively rapidly. The lattice constant of sphalerite is, of course, invariant in the two-phase S + W field, but the data are limited by the fact that the phase field is narrow. Hence, the number of data points at these two temperatures is small. As is evident in Fig. 2, the lattice constants for the two-phase mixtures in samples reacted at the lower temperatures (700 and 800 °C) continued to increase with increasing concentration of CdS, but not as rapidly as in the single-phase solid solution. This is probably due to the incomplete establishment of equilibrium. Consequently, the accuracy of the sphalerite solvus determined from the parametric method is not as valid as those at 900 and 950°C due to the variancy of the lattice constant values in the two-phase region. For this reason we relied on the disappearing phase method to determine the phase boundaries at the lower temperatures.
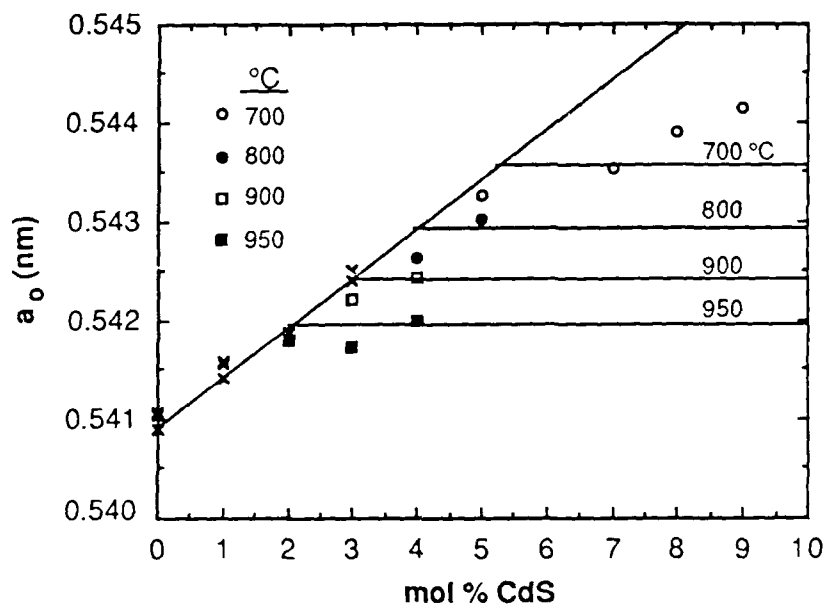

FIG. 2
The variation of the lattice constant of sphalerite, a_0, as a function of the
CdS content of the mixtures prepared. The points indicated by X apply to the
single phase solid solution of CdS in ZnS.

The parametric method was also used to determine the (S + W)/W phase boundary compositions at 900 and 950 °C. The c and a lattice constants both vary linearly with the CdS concentration in the single-phase wurtzite region, and the intersection between the horizontal and sloped lines is the solvus as shown in Fig. 3. The compositions of the wurtzite phase boundaries determined from both c and a parameters are consistent (~4 mol % CdS at 950 °C and 5.5 to 6 mol % CdS at 900 °C). The small number of data points determining the horizontal lines is due to the narrow compositional range of the two-phase field at these temperatures.

The disappearing phase method proved to be more reliable for determining the phase boundaries at the lower temperatures. The method is based upon the variation of the relative amounts of S and W along a tie-line in the two-phase field as the overall composition is changed (4). For example, the weight fraction of W should decrease to 0 as the composition approaches the S solvus, and since the intensity of a particular wurtzite peak, I_W, is proportional to the weight % W in the two-phase mixture, the ratio I_W/I_S should also approach a value of zero as the sphalerite solvus is reached (I_S is the intensity of a sphalerite peak). The solvus composition is determined from an extrapolation of the variation of I_W/I_S vs. weight % CdS to the zero ordinate value.
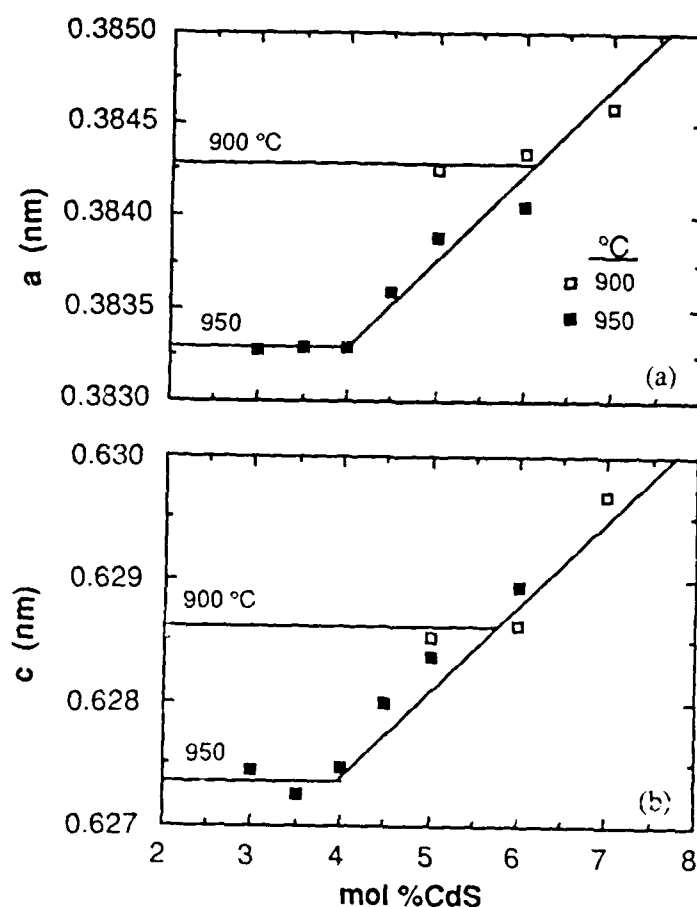
FIG. 3

Results obtained applying the parametric method; (a) illustrates the variation of the lattice constant a, while (b) illustrates the variation of the lattice constant c with the concentration of CdS.

The integrated intensities of the {311} sphalerite and the {$21\bar{3}1$} wurtzite peaks were chosen for this analysis. I_S and I_w were computed using a numerical analysis program, subtracting the contribution of $CuK\alpha_2$ radiation. Depending on the system being investigated, the relative ratio of the intensities can vary linearly or non-linearly with composition (4). From a cursory examination of the data, we decided to try a linear relationship and compare the results with the data in Fig.1. The data are shown in Fig. 4, where it is evident that the assumed linear behavior is better obeyed by the data in Fig. 4a than in Fig. 4b.

From a combination of the two analytical methods used, the partial phase diagram for the ZnS-CdS system over the temperature range of this study is shown in Fig. 5a. The solid curves drawn in Fig. 5a are shown in Fig. 5b, where they are superimposed on the data from Fig. 1; the agreement is very good. We are therefore confident that the results obtained using the disappearing phase method are accurate, despite the scatter in Fig. 4b. The disappearing phase method succeeded where the parametric method failed because the integrated intensities of the broad peaks in the two-phase mixtures are more accurately measured than the positions of the peak maxima.

The partial ZnS-CdS phase diagram determined over the temperature range 250 to 450 °C under hydrothermal conditions by Kaneko et al. (3) exhibits features similar to those in Fig. 5, especially insofar as the solubility of CdS in ZnS decreases with increasing temperature. Kaneko et al. made no attempt to determine the phase boundaries, but it is evident that their two-phase equilibria are shifted to higher mol % CdS, and the compositional range of their two-phase field is much greater. The two phase diagrams can be reconciled only if the sphalerite phase is stabilized

under hydrothermal conditions, but there is no convincing evidence to suggest that his stabilization process occurs. Cherin et al. (5) found a two-phase mixture of sphalerite and wurtzite in their ZnS single crystals containing 5 mol % CdS. Ther crystals were grown in a temperature gradient of 925 to 950 °C using the iodine vapor transport method. Their result is entirely consistent with our phase diagram.
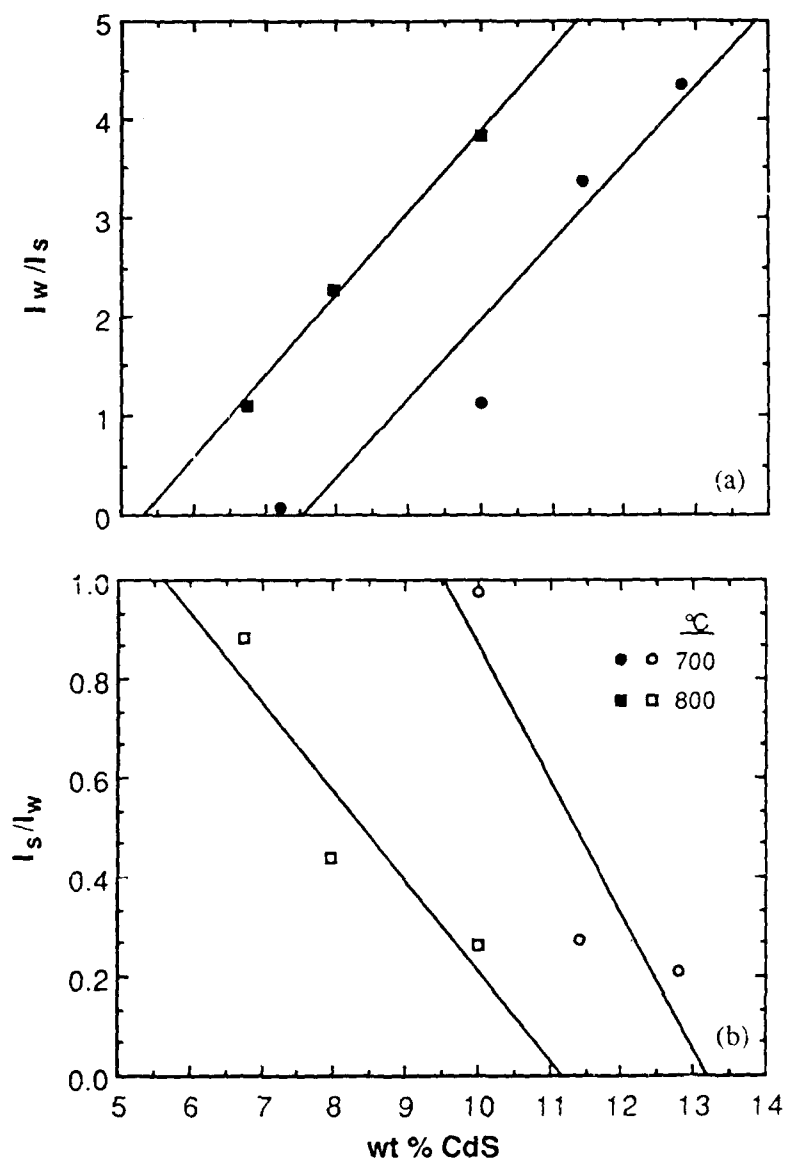

FIG. 4

Results obtained using the disappearing phase method: (a) The ratio of the intensities of the wurtzite {2131} peak and the sphalerite {311} peak, I_w/I_s, as a function of the concentration of CdS in weight %. In (b) the ratio of the intensities is inverted.

The use of differential thermal analysis for determination of the phase boundaries was attempted in several trial runs using pure ZnS. Since the enthalpy of the sphalerite to wurtzite transformation is 3.19 kcal/mol (6) in pure ZnS, the transition was not detected on heating and cooling

through 1020 °C. Thus,the small heat evolution during the transformation rendered thermal analysis ineffective for determining the phase diagram in this system.
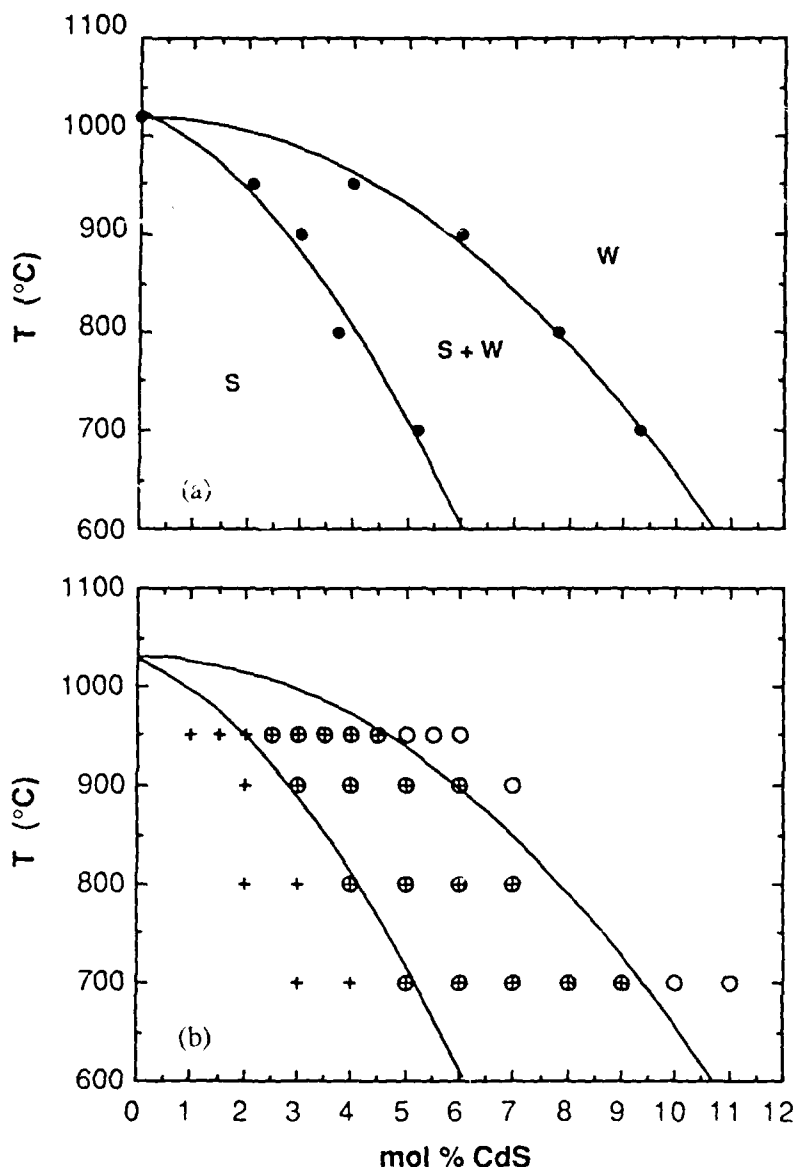

FIG. 5

(a) Partial phase diagram for the ZnS-CdS system over the temperature range 700 to 1100 °C. A comparison with the phases observed over the range of conditions in Fig. 1 is shown in (b).

Summary

The partial phase diagram for the ZnS-CdS system was determined over the temperature range 700 to 950 °C. Cubic and hexagonal solid solutions of ZnS were formed, and the boundaries of the two phase region were determined by the use of the parametric and disappearing phase methods.

Acknowledgement

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